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(54) Title: PESTICIDE OIL-IN-WATER-IN-OIL EMULSION

(57) Abstract: An oil-in-water-in-oil multiple emulsion, comprising an inner oily phase, an aqueous intermediate layer and an outer oily phase, which comprises one or more pesticides, is useful for controlling weeds, diseases and pests.

PESTICIDAL OIL-IN-WATER-IN-OIL EMULSION

The present invention relates to a method of preparing liquid formulations of pesticides in the form of an oil-in-water-in-oil multiple emulsion. These formulations are often "non classified" in terms of acute toxicity and may contain multiple, normally incompatible pesticides, in addition to their ability to increase the efficacy of the formulated pesticides.

Multiple emulsion technology is mainly used in the formulation of cosmetics, pharmaceuticals and cleaning products in order to provide prolonged active ingredient delivery systems.

EP-A-0,507,693 describes water-in-oil-in-water (W/O/W) cosmetic formulations using a perfluoropolyether as a medium oily layer, esters of sucrose as a hydrophilic emulsifier system, polyglyceryl methacrylate as a water soluble gelling agent and dodecylglycol polyethoxylated or lecithin as lipophilic emulsifier system. EP-A-0,614,660 describes another W/O/W cosmetic formulations for skin-care effects based on hydrophilic active ingredients, such as biolysat hafnia, UV filter, sodium lactate, and lipophilic active ingredients, such as UV filter, vitamin A palmitate, using aqueous gelling agents such as xanthan gum, carbomers, polyglyceryl methacrylate, and polyethoxylated hydrogenated castor oil as the lipophilic emulsifier system. EP-A-0,715,842 and EP-A-0,717,978 describe rinse-off W/O/W cream formulations for delivery of a topically-active ingredient to skin or hair, where cyclic volatile silicone compounds (e.g. cyclomethicone) are used as the medium oily layer and polyethoxylated and/or polypropoxylated ether of fatty acid (C_6 to C_{22}) alcohol are used as the lipophilic emulsifier system and a hydrophilic emulsifier capable of forming liquid crystals was optionally incorporated. US-A-4,931,210 relates to a process for producing cosmetic W/O/W multiple emulsions using a polyglycerol polyricinoleate as emulsifier and heating the water-in-oil (W/O) primary emulsion to 50 - 80°C. WO-A-99/707463 relates to W/O/W medicinal compositions, using dodecane as a medium oily layer, lecithin or polyethoxylated alkylamides as hydrophilic emulsifier system, polyvinylpyrrolidone, polyethyleneglycol (PEG) or

xanthan gum as water soluble thickeners and polyglyceryl polyricinoleate or lecithin as a lipophilic emulsifier system. Liquid controlled release formulations, such as microporous microcapsules, are provided by using W/O/W formulations as the support medium of the technology and subsequently removing an organic solvent from the same medium (US-A-4,857,335).

US-A-4,875,927 describes a process of preparing herbicidal W/O/W multiple emulsion comprising 75 g/l or more of a salt of a herbicidal bipyridylium diquaternary cation as an active ingredient. This multiple emulsion has a lower oral toxicity than conventional aqueous formulations and incorporate a condensate of p-nonylphenol with propylene oxide and ethylene oxide as hydrophilic emulsifier system and a block co-polymer of poly-12-hydroxy stearic acid and polyethoxylated or a reaction product of polyisobutylene succinic anhydride and ethanolamine as lipophilic emulsifier.

EP-A-0,391,124 relates to an oil-in-water-in-oil (O1/W/O2) cosmetic formulation with skin-care effect, using a ceramide fat as inner oily phase (O1), fatty acid esters of polyethoxylated sorbitan or sucrose as hydrophilic emulsifier system, polyol as a water soluble humectant, phospholipides or polydimethylsiloxanes as a lipophilic emulsifier system and polysiloxanes as the outer oily phase (O2). EP-A-0,559,013 describes other O1/W/O2 cosmetic formulations using polyglycerol ricinoleate as the hydrophilic emulsifier system and polyoxyalkylene polysiloxanes as the lipophilic emulsifier system.

Conventional pesticide formulations, especially with insecticides, can sometimes exhibit a rather high acute oral toxicity and severe irritation to skin and eyes. Besides this, it is often a problem to co-formulate two or more active ingredients of pesticides, which can not be formulated directly together due to their chemical and/or physical properties (i.e. risk of decomposition).

Tadros in Colloidal Aspects of Pesticidal and Pharmaceutical Formulations - An Overview, Pesticide Science, 26 (1), p. 72-73 (1989) suggests a two-stage manufacture process for O/W/O formulations in which a primary oil-in-water

emulsion is then emulsified into oil at low shear to avoid inversion of the first emulsion. The constraint of low shear implies that the multiple droplets are fairly large with an average diameter of 30 to 50 microns.

It has now been found, that the present invention has overcome the above mentioned problems for pesticides and that additionally an increase in the efficacy of the formulated pesticides could be detected. A stable formulation was achieved by using high shearing effects in the final preparation step, which reduced the size of the multiple droplets.

The invention is characterized by an oil-in-water-in-oil multiple emulsion (O1/W/O2) with a multiple droplet size of less than 25 microns, preferably in the range of 3 to 24 microns, which comprises of an inner oily phase (O1), an aqueous intermediate layer (W) and an outer oily phase (O2) and which comprises one or more pesticides. Preferably the inner oily phase or the inner and outer oily phase comprises one or more pesticides.

'Multiple droplet' as used herein means the water droplet (W) containing emulsified droplets of the inner oily internal phase (O1).

The inner oily phase (O1) generally comprises an organic solvent having an acute oral LD 50 toxicity value for rats higher than 2000 mg/kg body weight, a molecular weight lower than 500, preferably lower than 240, and a cinematic viscosity, measured in all cases at 20°C with a rotation viscometer, lower than 20 mm^2/sec, preferably less than 5 mm^2/sec, where LD 50 is the dose, which causes 50 % mortality of the tested animals.

The inner oily phase (O1) preferably comprises an oil from the group of:

a) vegetable and/or animal oils, which may be a mixture of fatty acids, and their esterified forms, such as

fatty esters, resulting from the reaction between vegetable and/or animal oils, such as coconut oil, rape oil, sunflower oil, cotton oil, maize oil, linseed oil, palm oil, palm kern oil, soya oil, thistle oil, castor oil, tallow oil, beef tallow and C_1 to C_5 alcohols, preferably C_1 to C_3 alcohols, such as methyl, ethyl, n-propyl, isopropyl alcohol; aliphatic esters, preferably with methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and esters of fatty acids, preferably C_1 to C_{18} fatty acids, such as caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, oleic acid and mixtures thereof and preferably mixtures of caprylic and capric acids methyl esters (e.g. ®Radia 7983, Fina Chemicals, Belgium);

b) acid esters, including mono-, di- and tri-esters, such as ester derivatives of lactic acid, preferably lauryl lactate and/or 2-ethyl hexyl lactate, adipic acid, preferably as diisopropyl adipate (e.g. ®Crodamol DA, Croda Oleochemicals, UK) and diisobutyl adipate;
citric acid, preferably tributyl citrate and/or acetyl tributyl citrate, glutaric acid, succinic acid, preferably dibasic esters, more especially mixtures of methyl esters of adipic, glutaric and/or succinic acids;

c) terpenes, such as d-limonene.

The organic solvents for the inner oily phase (O1) are optinally, depending on chemical and/or physical properties of the pesticides, combined with ketones, such as 2-heptanone, n-octyl pyrrolidone, n-dodecyl pyrrolidone, acetophenone and/or cyclohexanone to ensure that the active ingredients stays in the inner oily phase (O1).

The inner oily phase (O1) optionally comprises further additives and/or auxiliaries: e.g.

a) one or more non ionic hydrophilic emulsifiers, preferably non ionic hydrophilic emulsifiers having a HLB number in the range of 9 to 12, especially 11 to 11.5, more preferred from the group of polyethoxylated derivatives, preferably 5 and/or 6 EO

(EO means an ethylene oxide unit) moles, of fatty alcohols, such as oleic alcohol (e.g. ®Volpo N5, Croda Oleochemicals, UK, main component oleic alkohol polyethoxylated –(5)-) and/or castor oil and polyethyleneglycol with a molecular weight of about 400 (PEG 400), fatty acid esters, such as oleates, especially PEG 400 monooleate (e.g. ®Radiasurf 7403, Fina Chemicals, Belgium; ®Cithrol 4 MO, Croda Oleochemicals, UK).

HLB is the abbreviation for hydrophilic-lipophilic-balance, as described by Griffin, J. Soc. Cosmet. Chem 1, 34 (1949) and 5, 249 (1954).

b) one or more antifreeze agents, preferably of diols, monopropylene glycol, hexylene glycol, urea and/or sugar derivatives thereof.

c) one or more pesticide stabilising agents preferably acetic acid, citric acid, 2,6-di-tert.-butyl-4-(dimethylaminomethyl)phenol, 2-tert.-butyl-4-methoxyphenol and 3-tert.-butyl-4- methoxyphenol.

The outer oily phase (O2) generally comprises a mineral oil having an acute oral LD 50 toxicity value for rats higher than 2000 mg/kg body weight, preferably higher than 5000 mg/kg, a distillation range from 200°C to 350°C, preferably 230°C to 310°C, a cinematic viscosity higher than 5 mm^2/s and lower than 50 mm^2/sec, preferably from 10 to 30 mm^2/sec, and an average molecular weight of 200 to 400, preferably 230 to 320.

Examples of such mineral oils for the outer oily phase (O2) include:

a) light grade polyisobutenes, such as ®Napvis X10 and ®Napvis X35 (both from BP Chemicals, main component polyisobuten);

b) isoparaffins, such as ®Isopar V (Exxon, main component isoparaffin);

c) C_5-, C_6-, C_7- cycloparaffins, such as ®Nyflex 800 and ®Nytex 801 (both from Nynas, main components cycloparaffins).

The outer oily phase (O2) optionally comprises further additives and/or auxiliaries such as non ionic lipophilic emulsifiers preferably having a molecular weight higher than 500: e.g.

a) a non ionic lipophilic emulsifier having an HLB number of 4.5 to 7, preferably 6 to 6.5, preferably oleic derivatives and/or glycerol derivatives, more preferably a combination of them, such as glycerol dioleate and/or trioleate, glycerol olostearate (polyethoxylated or not), polyglycerol polyoleate, such as triglycerol monooleate (e.g. ®Drewpol 3.1.0, Stepan), tetraglycerol tetraoleate, decaglycerol tetraoleate (e.g. ®Drewpol 10.4.0, Stepan), decaglycerol octaoleate, decaglycerol decaoleate, especially tetraglycerol tetraoleate (e.g. ®Witconol 14, CK Witco, USA),

b) a second non ionic lipophilic emulsifier, preferably a block co-polymer of poly-12-hydroxy stearic acid and/or polyalkylene glycol, such as ®Atlox 4912 (Uniquema), and/or random polymeric structure compounds (tridimensional networks) synthesized from polyols, polyethylenglycol, aliphatic carboxylic acids, aliphatic polycarboxylic acids and/or anhydrides, such as ®Atlox 4914 (Uniquema).

Light grade polybutenes as described above are preferably manufactured from a wholly aliphatic mixed C_4 feedstock consisting essentially of iso-butene with n-butenes.

Light napthenic distillates, such as cycloparaffins, as described above are preferably manufactured from a Venezuelan heavy naphtenic feedstock free from n-paraffins and consisting essentially of bitumen and heavy distillates.

Isoparaffinic structure as described above are pure synthetic products .

Pesticides, as active ingredients, are disclosed in the 'The Pesticide Manual', 12th Ed., Editor: C D S Tomlin, British Crop Protection Council, Farnham 2000, especially insecticides, acaricides, nematicides, fungicides, herbicides, plant growth regulators, rodenticides and anthelminthics, preferably insecticides, more preferred insecticides selected from the group of:

neonicotinoids, e.g. imidacloprid, acetamiprid, thiamethoxam, thiacloprid, tefuranitozine, clothianidin;
carbamates, e.g. triazamate, aldicarb, thiodicarb, formetanate, carbaryl, pirimicarb;
pyrethroids, e.g. acrinathrin, tralomethrin, fenvalerate, lambda-cyhalothrin, tefluthrin, etofenprox, cypermethrin, deltamethrin;
organophosphates, e.g. triazophos, ethoprofos;
fiproles, e.g. fipronil, ethiprole;
cyclodienes, e.g. endosulfan;
benzhydrazides, e.g. tebufenozid.

The following terms and/or abbreviations are used to describe the invention: oil-in-water-in-oil multiple emulsion (O1/W/O2), which is a synonym for the oil-in-water-in-oil formulation (O/W/O); the inner oily phase (O1), the aqueous phase (Wp), which results in the aqueous intermediate layer (W); the inner oil-in-water emulsion (O1/W) and the outer oily phase (O2).

In the preferred oil-in-water-in-oil multiple emulsion (O1/W/O2):

the inner oily phase (O1) is in the range of 15 to 50 % (w/w), preferably 20 to 37 % (w/w);

the non ionic hydrophilic emulsifier or a mixture thereof is in the range of 1.5 to 5 % (w/w), preferably 2.0 to 2.5 % (w/w);

the antifreeze agent is in the range of 1 to 3.5 % (w/w), preferably 1.5 to 2.5 % (w/w);

the pesticide stabilising agent is in the range of 0.01 to 0.2% (w/w);

the aqueous intermediate layer is in the range of 10 to 35% (w/w), preferably 15 to 25 % (w/w);

the outer oily phase (O2) is in the range of 30 to 60 % (w/w), preferably 35 to 55 % (w/w);

the non ionic lipophilic emulsifier or a mixture thereof is in the range of 3 to 7 % (w/w), preferably 3 to 5%.

The concentration of pesticides in the oil-in-water-in-oil multiple emulsion (O1/W/O2) is preferably 0.01 to 100 g active ingredient/l, e.g. 0.05 to 50 g active ingredient/l.

The oil-in-water-in-oil multiple emulsions (O1/W/O2), according to the invention, are often "non classified" in terms of acute toxicity. They can contain multiple, formerly incompatible active ingredients, which could not be formulated directly together due to their chemical and/or physical properties (e.g. risk of decomposition). Additionally, these oil-in-water-in-oil multiple emulsions (O1/W/O2) enhance biological activity with respect to speed and dosage compared with standard formulations.

Besides this, the oil-in-water-in-oil multiple emulsions (O1/W/O2) are still liquid, which allows e.g. low and/or ultra low volume spray applications, and which are considered by customers as a safe and convenient way to protect widely crops against different types of weeds, diseases and pests, where a mixture of suitable pesticides is needed.

The process for the manufacture of an emulsion (O1/W/O2) according to the invention usually comprises two steps:

The first step is the preparation of an inner oil-in-water emulsion (O1/W), comprising

a) preparation of an inner oily phase (O1) by dissolving one or more pesticides in one or more organic solvents followed by the addition of one or more non ionic hydrophilic emulsifiers, which promotes the formation of an inner oil-in-water emulsion (O1/W), by using low shearing mixing effects, carried out by a mixer (e.g. paddle agitator).

b) preparation of an aqueous phase (Wp), preferably obtained by dissolving an one or more antifreeze agents at room temperature using low shearing mixing effects, preferably carried out by a mixer (e.g. paddle agitator). The mixing operation is maintained until a homogeneous aqueous solution is obtained.

c) preparation of an inner oil-in-water emulsion (O1/W), containing one or more pesticides, by dispersing, an inner oily phase (O1), obtained in a), in an aqueous phase (Wp), obtained in b), at room temperature using high shearing mixing effects, carried out for instance by Ultra-Dispenser stirrer, such as a rotor-stator mixer available from companies like Silverson (UK) and IKA (Germany). The mean diameter of the inner oily phase (O1) droplets, dispersed in an aqueous phase (Wp), should be lower than 1.5 microns to ensure later on a good and stable quality of the oil-in-water-in-oil multiple emulsion.

The second step is the preparation of a final oil-in-water-in-oil emulsion (O1/W/O2) by dispersing an inner oil-in-water emulsion (O1/W) from the fist step in an outer oily phase (O2) comprising the

d) preparation of an outer oily phase (O2), e.g. by dissolving one or more pesticides in one or more organic solvents followed by the addition of one or more lipophilic emulsifiers using low shearing mixing effects, carried out preferably by a mixer (e.g. paddle agitator), to promote the later formation of the water-in-oil emulsification, in which the dispersed phase is the inner oil-in-water emulsion (O1/W).

e) preparation of a final oil-in-water-in-oil emulsion (O1/W/O2) by dispersing an inner oil-in-water emulsion (O1/W), obtained in c), in an outer oily phase (O2), obtained in

d), at room temperature using high shearing mixing effects, carried out by Ultra-Dispenser stirrer, such as a rotor-stator mixer available from companies like Silverson (UK) and IKA (Germany) for high shearing mixing effects. The choice of the speed for the shearing mixing effects is crucial for the final size of the multiple droplets.

At the end of the manufacturing process the droplet average characteristics of an oil-in-water-in-oil multiple emulsion (O1/W/O2), containing one or more pesticides, are determined using a microscope.

The terms 'low shearing mixing effects' and 'high shearing mixing effects' used to explain the manufacture process of a multiple emulsion (O1/W/O2) according to the invention, correspond to different average sizes of the resulting multiple droplets. That means 30 to 50 microns when using 'low shearing', less than 25 microns (in the range of 3 to 24 microns) when involving 'high shearing'. The assessment of the mean diameter of the resulting multiple droplets is carried out by examination of an oil-in-water-in-oil multiple emulsion (O1/W/O2) sample under the microscope.

The invention also relates to:

a) a method of controlling weeds, diseases and pests, preferably for controlling harmful arthropods, especially insects, which comprises applying an effective amount of oil-in-water-in-oil emulsion (O1/W/O2), containing one or more pesticides, preferably insecticides, especially a pyrethroid, for treating and/or protecting crops, for instance in the form of a low volume and/or ultra low volume and/or oily dilution.

b) the use of oil-in-water-in-oil emulsion (O1/W/O2), containing one or more pesticides, preferably insecticides, especially a pyrethroid, as a formulation in crop protection, which could be applied for treatment and/or protection of crops, for instance by diluting the oil-in-water-in-oil emulsion (O1/W/O2) with an oily thinner, e.g. ®Norpar 15 (Exxon, main component paraffin), prior to application.

The present invention is illustrated by the following examples, without limiting the invention thereto.

The cited substances are defined as follows: ®Radia 7983 (mixture of methyl ester of caprylic and capric acid; manufacturer (Mfc) Total Fina); ®Crodamol DA, diisopropyl adipate; Mfc Croda); ®Volpo N5 (oleic alkohol polyethoxylated –(5)- Mfc Croda); ®Radiasurf 7403 (PEG 400 monooleat; Mfc Total Fina); ®Cithrol 4 MO (PEG 400 monooleat; Mfc Croda); ®Napvis X10 and ®Napvis X35 (polyisobuten; Mfc BP Chemicals); ® Isopar V (isoparaffin; Mfc Exxon); ®Nyflex 800 and ®Nytex 801 (cycloparaffins; Mfc Nynas); ®Drewpol 3.1.0 (triglycerol monooleat; Mfc Stepan); ®Drewpol 10.4.0 (decaglycerol tetraoleat; Mfc Stepan); ®Witconol 14 (tetraglycerol tetraoleat; Mfc Witco); ®Atlox 4912 and ®Atlox 4914 (Mfc Uniquema); ®Norpar 15 (paraffin; Mfc Exxon).

Preparation examples

Example 1:

Components of Multiple Emulsion (O1/W/O2)	Ingredients	Concentration % (w/w)
Active Ingredient	deltamethrin	0.625
Solvent (Inner Oily Phase, O1)	®Radia 7983	36.575
Non Ionic Hydrophilic Emulsifier	®Radiasurf 7403	2.230
Aqueous Intermediate Layer (W)	Water	20.000
Non Ionic Lipophilic Emulsifier	®Atlox 4914	1.000
Non Ionic Lipophilic Emulsifier	®Witconol 14	3.000
Solvent (Outer Oily Phase, O2)	®Nyflex 800	36.570

Example 2:

Components of Multiple Emulsion (O1/W/O2)	Ingredients	Concentration % (w/w)
Active Ingredient	acrinathrin	0.125
Solvent (Inner Oily Phase, O1)	®Radia 7983	19.875
Non Ionic Hydrophilic Emulsifier	®Radiasurf 7403	2.230
Aqueous Intermediate Layer (W)	Water	20.000
Non Ionic Lipophilic Emulsifier	®Atlox 4914	1.000
Non Ionic Lipophilic Emulsifier	®Witconol 14	3.000
Solvent (Outer Oily Phase, O2)	®Nyflex 800	53.770

Example 3:

Components of Multiple Emulsion (O1/W/O2)	Ingredients	Concentration % (w/w)
Active Ingredient	endosulfan	0.625
Solvent (Inner Oily Phase, O1)	®Radia 7983	36.575
Non Ionic Hydrophilic Emulsifier	®Radiasurf 7403	2.230
Aqueous Intermediate Layer (W)	Water	20.000
Non Ionic Lipophilic Emulsifier	®Atlox 4912	0.750
Non Ionic Lipophilic Emulsifier	®Witconol 14	3.250
Solvent (Outer Oily Phase, O2)	®Nyflex 800	36.570

Example 4:

Components of Multiple Emulsion (O1/W/O2)	Ingredients	Concentration % (w/w)
Active Ingredient	deltamethrin	0.625
Solvent (Inner Oily Phase, O1)	®Radia 7983	36.575
Non Ionic Hydrophilic Emulsifier	®Radiasurf 7403	2.230
Aqueous Intermediate Layer (W)	Water	20.000
Non Ionic Lipophilic Emulsifier	®Atlox 4914	1.000
Non Ionic Lipophilic Emulsifier	®Witconol 14	3.000
Solvent (Outer Oily Phase, O2)	®Napvis X35	36.570

Example 5:

Components of Multiple Emulsion (O1/W/O2)	Ingredients	Concentration % (w/w)
Active Ingredient	fipronil	0.625
Solvent (Inner Oily Phase, O1)	®Radia 7983	36.575
Non Ionic Hydrophilic Emulsifier	®Radiasurf 7403	2.230
Aqueous Intermediate Layer (W)	Water	18.000
Antifreeze Agent	monopropylene-glycol	2.000
Non Ionic Lipophilic Emulsifier	®Atlox 4914	1.000
Non Ionic Lipophilic Emulsifier	®Witconol 14	3.000
Solvent (Outer Oily Phase, O2)	®Nyflex 800	36.570

Biological examples

Example 1: Efficacy of deltamethrin formulations on Heliothis virescens

The efficacy of deltamethrin in different formulations was tested by spraying cotton plants (200 l/ha) infested with Heliothis virescens (tomato budworm). For each formulation type and deltamethrin dosage two independent trials, with 20 larvae each, were conducted. Assessment of mortality, as an indicator of activity, was carried out 24 hours after application. Average values (% dead larvae) are shown below.

Results

Formulation type	Active ingredient and application dosage	Assessment time after application (hours)	Mortality (% dead larvae)
EC 25 g/l (Standard formulation) in Water [1)]	deltamethrin (10 g/ha)	24	100
	deltamethrin (3 g/ha)	24	70
	deltamethrin (1 g/ha)	24	43
SC 50 g/l (Standard formulation) in Water [1)]	deltamethrin (10 g/ha)	24	100
	deltamethrin (3 g/ha)	24	85
	deltamethrin (1 g/ha)	24	68
O/W/O 1.25 g/l (Oil-in-water-in-oil formulation) in Paraffin [2)]	deltamethrin (10 g/ha)	24	100
	deltamethrin (3 g/ha)	24	100
	deltamethrin (1 g/ha)	24	65
O/W/O 1.25 g/l (Blank formulation)	No active ingredient	24	15
Untreated control Paraffin (®Norpar 15) [2)]	No active ingredient	24	20
Untreated control Water [1)]	No active ingredient	24	0

An increase of activity is seen with the use of the oil-in-water-in-oil O/W/O 1.25 g/l formulation compared to the use of standard EC 25 g/l and SC 50 g/l formulations.

Example 2: Efficacy of deltamethrin formulations on Spodoptera littoralis

Example 1 was repeated, replacing Heliothis virescens with Spodoptera littoralis (Egyptian cotton leafworm). Assessment of mortality was carried out 24 hours or 48 hours after application. Results are shown below.

Results

Formulation type	Active ingredient and application dosage	Assessment time after application (hours)	Mortality (% dead larvae)
EC 25 g/l (Standard formulation) in Water [1)]	deltamethrin (10 g/ha)	48	100
	deltamethrin (3 g/ha)	48	75
	deltamethrin (1 g/ha)	48	30
SC 50 g/l (Standard formulation) in Water [1)]	deltamethrin (10 g/ha)	48	100
	deltamethrin (3 g/ha)	48	80
	deltamethrin (1 g/ha)	48	28
O/W/O 1.25 g/l (Oil-in-water-in-oil formulation) in Paraffin [2)]	deltamethrin (10 g/ha)	24	100
	deltamethrin (3 g/ha)	24	100
	deltamethrin (1 g/ha)	24	60
O/W/O 1.25 g/l (Blank formulation)	No active ingredient	24	20
Untreated control Paraffin (®Norpar 15) [2)]	No active ingredient	24	20
Untreated control Water [1)]	No active ingredient	48	0

Again, an increase in activity is seen with the use of the oil-in-water-in-oil O/W/O 1.25 g/l formulation compared to the use of the standard EC 25 g/l and SC 50 g/l formulation. Additionally the speed of activity is enhanced by the use of the oil-in-water-in-oil O/W/O 1.25 g/l formulation, which achieved higher control after 24 hours compared with the standard EC 25 g/l and SC 50 g/l formulations after 48 hours.

Claims

1. An oil-in-water-in-oil multiple emulsion with a multiple droplet size of less than 25 microns, comprising an inner oily phase, an aqueous intermediate layer and an outer oily phase, which comprises one or more pesticides.

2. An oil-in-water-in-oil multiple emulsion according to claim 1, wherein the inner oily phase or the inner and outer oily phase comprises one or more pesticides.

3. An oil-in-water-in-oil multiple emulsion according to claim 1 or 2, wherein the pesticide is from the group of insecticides, acaricides, nematicides, fungicides, herbicides, plant growth regulators, rodenticides and anthelminthics.

4. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 3, comprising an insecticide from the group of neonicotinoids, carbamates, pyrethroids, organophosphates, fiproles, cyclodienes and benzhydrazides.

5. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 4, wherein the concentration of the pesticide is 0.01 to 100 g active ingredient/l.

6. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 5, wherein the inner oily phase comprises one or more pesticide stabilising agents.

7. An oil-in-water-in-oil multiple emulsion according to claim 6, wherein the pesticide stabilising agent is acetic acid, citric acid, 2,6-di-tert.-butyl-4-(dimethylaminomethyl-)phenol, 2-tert.-butyl-4-methoxyphenol or 3-tert.-butyl-4-methoxyphenol.

8. An oil-in-water-in-oil multiple emulsion according claims 6 and/or 7, wherein the content of the pesticide stabilising agent is in the range of 0.01 to 0.2% (w/w).

9. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 8, wherein the inner oily phase comprises a solvent from the group of organic solvents having an acute oral LD 50 toxicity value for rats higher than 2000 mg/kg body weight, a molecular weight lower than 500 and a cinematic viscosity, measured at 20°C with a rotation viscometer, lower than 20 mm^2/sec.

10. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 9, wherein the organic solvents are vegetable oils and/or animal oils, acid esters and/or terpenes.

11. An oil-in-water-in-oil multiple emulsion according to claim 9 and/or 10, wherein the organic solvents for the inner oily phase comprise one or more ketones.

12. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 11, comprising 15 to 50 % (w/w) of the inner oily phase.

13. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 12, wherein the inner oily phase comprises one or more non ionic hydrophilic emulsifiers, from the group of polyethoxylated derivatives of fatty alcohols.

14. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 13, wherein the content of the non ionic hydrophilic emulsifier or a mixture thereof is in the range of 1.5 to 5 % (w/w).

15. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 14, comprising 10 to 35% (w/w) of the aqueous intermediate layer.

16. An oil-in-water-in-oil multiple emulsion according to any one of claim 1 to 15, wherein the aqueous intermediate layer comprises one or more antifreeze agents.

17. An oil-in-water-in-oil multiple emulsion according to claim 16, wherein the content of the antifreeze agent is in the range of 1 to 3.5 % (w/w).

18. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 17, wherein the outer oily phase comprises a mineral oil having an acute oral LD 50 toxicity value for rats higher than 2000 mg/kg, a distillation range from 200°C to 350°C, a cinematic viscosity, measured at 20°C with a rotation viscometer, higher than 5 and lower than 50 mm^2/sec, and an average molecular weight of 200 to 400.

19. An oil-in-water-in-oil multiple emulsion according to claim 18, wherein the mineral oil is a light grade polyisobutene, isoparaffin and/or C_5 to C_7 cycloparaffin.

20. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 19, comprising 30 to 60 % (w/w) of the outer oily phase.

21. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 20, wherein the outer oily phase comprises non ionic lipophilic emulsifiers having a molecular weight higher than 500.

22. An oil-in-water-in-oil multiple emulsion according to any one of claims 1 to 21, wherein the content of non ionic lipophilic emulsifier or a mixture thereof is in the range of 3 to 7 % (w/w).

23. A process for the manufacture of an oil-in-water-in-oil emulsion according to any one of claims 1 to 22, which comprises,

a) the preparation of an inner oil-in-water emulsion, which is obtained by dispersing using high shearing mixing effects, an inner oily phase, obtained by dissolving one or more pesticides in one or more organic solvents optionally followed by the addition of one or more non ionic hydrophilic emulsifiers using low shearing mixing effects, in an aqueous phase, optionally obtained by dissolving one or more antifreeze agents using low shearing mixing effects, and

b) the preparation of a final oil-in-water-in-oil emulsion by dispersing an inner oil-in-

water emulsion using high shearing mixing effects, in an outer oily phase, optionally obtained by dissolving one or more pesticides in one or more organic solvents followed by the addition of one or more lipophilic emulsifiers using low shearing mixing effects.

24. A method of controlling weeds, diseases and pests, which comprises applying an oil-in-water-in-oil emulsion according to any one of claims 1 to 23.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/04595

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N25/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	TH.F.TADROS: "Colloidal aspects of pesticidal and Pharmaceutical Formulations-An Overview" PESTIC. SCIENCE, vol. 26, no. 1, 1989, pages 51-77, XP000080613 Barking, Essex, GB page 72, last paragraph page 73, paragraph 1 ---	1-3,23, 24
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search	Date of mailing of the international search report
30 July 2002	12/08/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Nopper-Jaunky, A

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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